Benchmark configuration interaction spectroscopic constants for $X\,^1\Sigma_g^+$ C$_2$ and $X\,^1\Sigma^+$ CN$^+$

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Explicit full configuration interaction (FCI) computations in a double-ζ plus polarization (DZP) basis, involving as many as 105 million Slater determinants, have been performed to sample the potential energy curves of $X\,^1\Sigma_g^+$ C$_2$ and $X\,^1\Sigma^+$ CN$^+$ for benchmark purposes. Quartic force fields have been determined at the optimized structures, and sets of anharmonic spectroscopic constants $[r_e,\ \omega_e,\ B_e,\ \bar{D}_e,\ \alpha_e,\ \text{and}\ \omega_e x_e]$ have been ascertained. Analogous results obtained from high-level but inexact correlation treatments establish a CISDTQ<CCSDT<CISDTQPH$\approx$FCI series of increasing accuracy for the notorious $X\,^1\Sigma_g^+$ C$_2$ and $X\,^1\Sigma^+$ CN$^+$ multireference systems. The data also reveal that recent schemes for CI+PT extrapolations to the FCI limit are quite accurate, to within 0.4 mE_h, 0.001 Å, and 4 cm^{-1} in the total energy, r_e, and ω_e, respectively. Whether such schemes approximate FCI curves with sufficient smoothness to reproduce the anharmonic data obtained here is elevated as a challenge for future work. © *1998 American Institute of Physics.* [S0021-9606(98)00416-4]

INTRODUCTION

Achieving the full configuration interaction (FCI) limit has been a persistent goal of molecular quantum mechanics, but for most chemical systems explicit FCI computations are intractable due to their factorial growth with respect to the one-particle basis and the number of electrons. In 1996, Evangelisti and co-workers[1] were the first to converge an explicit FCI wave function with over one billion determinants, although the feasibility of iterations toward this milestone had been demonstrated 6 years earlier.[2] The timings of their out-of-core vectorized and distributed-memory parallelized code presaged FCI computations involving over 10^{10} determinants. Shortly thereafter, Wulfov[3] claimed to pass the one quadrillion (10^{12} determinants) mark in FCI extrapolations on a personal computer, a powerful contribution indeed if the proposed CI+PT scheme proves to be a reliable estimator of exact FCI energies. Subsequent work[4] reported CI+PT energies, equilibrium geometries, and harmonic vibrational frequencies for a series of diatomic molecules, including F$_2$, BF, C$_2$, CN$^+$, and NO$^+$, in a DZP basis. These results were used to calibrate high-level theoretical methods such as configuration interaction through quadruple substitutions (CISDTQ) and complete coupled cluster through triple excitations (CCSDT), but confirmations by means of explicit FCI data were not possible.

The Wulfov work[3,4] is representative of the immense literature advocating configuration selection schemes for systematic approaches to the FCI limit. It has long been recognized that the FCI Hamiltonian matrix is very sparse and that perturbation theory can be used to evaluate/estimate contributions for myriad, unimportant configurations.[5–13] Contem-

porary CI+PT methods[3,14,15] are akin to the original two-class CIPSI approach[6] developed in 1973. The Hamiltonian is first diagonalized in an initial internal subspace to obtain multiconfigurational zeroth-order solutions (E_0,Ψ_0), and then within the remaining external space of Slater determinants (Φ_I), or alternatively configuration state functions (CSFs), the perturbation formula $\rho_I=\langle\Psi_0|H|\Phi_I\rangle^n(E_0-H_{I,I})^{-1}$ is used to compute contributions (ρ_I) to either the first-order wave function (CIPSI, $n=1$) or the second-order energy (CI+PT, $n=2$). All Φ_I with $|\rho_I|$ greater than a selected threshold (η) are then added to the internal space, and the process is repeated until self-consistency is achieved or the internal space becomes prohibitively large. In both CIPSI and CI+PT schemes, the final energy (E_η) is thus comprised of an exact solution within a self-consistent internal space plus perturbational corrections for the residual external space; the FCI limit is estimated by extrapolating E_η sequences to zero threshold. The CIPSI-3 variant partitions the external space into two classes based on a second threshold (τ), the treatment of the intermediate space satisfying $\eta>|\rho_I|>\tau$ being improved past second order either by variational means[7,16,17] or by fourth-order perturbation theory.[7] Continuing advances have extended the CIPSI methodology to direct CI algorithms[17–19] and size-consistent dressing of the Hamiltonian.[20] The wave function operator (WFO) approach of Wulfov and co-workers[3,15] is an efficient reformulation of the CI+PT method based on Slater determinants rather than configuration state functions.[14]

Another established configuration selection approach is the MRD-CI method of Buenker and Peyerimhoff.[10,11] In this treatment the reference space is chosen *a priori* rather than iteratively, customarily involving only the chemically important valence orbitals, and a selection scheme is used to approximate the associated multireference CISD energy. The single and double substitutions are winnowed by adding each

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TABLE I. DZP configuration interaction spectroscopic constants of $X\ ^1\Sigma_g^+$ C$_2$ and $X\ ^1\Sigma^+$ CN$^+$.[a]

	C$_2$					CN$^+$				
	CISDTQ	CCSDT	CISDTQPH	FCI	Expt.[b]	CISDTQ	CCSDT	CISDTQPH	FCI	Expt.[b]
r_e	1.2650	1.2675	1.2694	1.2695	1.2425	1.1975	1.1993	1.2010	1.2012	1.1729
B_e	1.7558	1.7490	1.7437	1.7433	1.8198	1.8192	1.8136	1.8085	1.8081	1.8964
ω_e	1842.5	1829.1	1814.6	1813.4	1854.7	2000.8	1988.4	1974.5	1973.6	2033.1
$\omega_e x_e$	13.00	12.57	13.28	13.19	13.34	14.81	15.04	15.67	15.71	16.14
$\bar{D}_e$	0.6377	0.6397	0.6441	0.6444	0.692	0.6015	0.6035	0.6069	0.6070	0.7
α_e	0.01668	0.01652	0.01698	0.01699	0.01765	0.01787	0.01813	0.01838	0.01838	0.0188
f_{rr}	12.0014	11.8265	11.6398	11.6251	12.1606	15.2425	15.0531	14.8442	14.8307	15.5737
f_{rrr}	−75.77	−74.08	−73.97	−73.89	−77.73	−106.96	−106.42	−105.64	−105.56	−111.55
f_{rrrr}	353	350	343	346	366	559	559	540	538	539

[a]Bond distances (r_e) in Å; harmonic frequencies (ω_e) in cm^{-1}; rotational (B_e), vibration-rotation interaction (α_e), and anharmonicity ($\omega_e x_e$) constants in cm^{-1}; quartic centrifugal distortion parameters ($\bar{D}_e$) in 10^{-5} cm^{-1}; quadratic (f_{rr}), cubic (f_{rrr}), and quartic (f_{rrrr}) force constants in aJ Å^{-2}, aJ Å^{-3}, and aJ Å^{-4}, respectively.
[b]Reference 38.

separately to the (relatively small) reference space and comparing the recomputed CI energy to an energy-lowering threshold. Hence, the multireference excitation space is partitioned into an internal space subjected to a final, large configuration interaction treatment, and an external space whose effects are quantified by Brillouin–Wigner perturbation theory. In 1995, Krebs and Bruenker[21] reported a new table-direct CI algorithm capable of handling MRD-CI internal spaces up to several hundred thousand determinants.

In 1989, Knowles[22] introduced an algorithm for FCI computations in which the expansion vectors ($\mathbf{b}_i$) of the Davidson method[23] are artificially made much sparser and left in nonorthogonal form, thus reducing both storage requirements and arithmetic operations. Converged CI energies are obtained as a function of diminishing thresholds for discarding elements of both $\mathbf{b}_i$ and $\boldsymbol{\sigma}_i (=\mathbf{H}\mathbf{c}_i)$ vectors, giving a series which approaches the numerically complete FCI result. The algorithm was hailed[24] as means of unlimited FCI calculations. A similar method is the dynamic CI approach of Mitrushenkov,[25,26] which employs a two-vector, nonorthogonal Davidson scheme[2,23,25] and discards determinants at each iteration simply according to their magnitude in the current CI vector. The zero threshold energy (ZTE) extension of the method essentially entails a single, numerically complete Davidson update on the final dynamic CI result for each cutoff. Recently, Mitrushenkov[27] has also performed dynamic CI+ZTE in a restricted internal space and treated external space contributions via second-order perturbation theory.

A valuable benchmark computation for testing these selective CI methods is the FCI energy of NH$_3$ in an ANO basis of DZP quality. With their sparse diagonalization algorithm, Knowles and Handy[24] first proposed an energy of $-56.4236\pm0.0001\ E_h$, but lower results were later found both in a CIPSI study[28] ($-56.423\ 825\ E_h$) and unpublished, selected CI work by Mitrushenkov and Amos ($-56.423\ 93\ E_h$).[29] This controversy was finally resolved by two independent determinations[30,31] of an even lower exact FCI energy ($-56.424\ 007\ E_h$). This example shows that schemes for approaching the FCI limit may suffer from

unexpectedly large contributions by the multitudinous neglected determinants.

In this letter we report high-order benchmark correlation treatments (CISDTQ, CCSDT, CISDTQPH, and FCI) for the problematic multireference electronic structures of ground-state C$_2$ and CN$^+$, two of the species investigated by Wulfov.[4] Unlike most other studies of this kind, our work is concerned with the correlation convergence of not only the total energy, r_e, and ω_e, but also higher derivatives of the potential energy curves and anharmonic spectroscopic constants. The performance of selective CI techniques is also addressed in comparison to the exact FCI method with a view toward both accuracy and smoothness criteria desirable for extrapolation schemes.

COMPUTATIONAL DETAILS

In this study a DZP basis was employed which is comprised of standard Huzinaga–Dunning[32] double-ζ sp sets augmented with Cartesian d-type polarization manifolds on the carbon [$\alpha_d(\text{C})=0.75$] and nitrogen [$\alpha_d(\text{N})=0.80$] atoms. The basis consists of 32 contracted Gaussian functions for both C$_2$ and CN$^+$, the contraction scheme being C($9s5p1d/4s2p1d$) and N($9s5p1d/4s2p1d$). The carbon and nitrogen $1s$ core and corresponding virtual (canonical Hartree–Fock) orbitals were frozen in all correlation treatments, thus allowing a direct comparison to previous work.[4,33] The resulting CI wave functions for $X\ ^1\Sigma_g^+$ C$_2$ contained 582 455 (CISDTQ), 16 786 215 (CISDTQPH), and 52 407 353 (FCI) determinants in D_{2h} symmetry, while those for $X\ ^1\Sigma^+$ CN$^+$ contained 1 164 439 (CISDTQ), 33 569 231 (CISDTQPH) and 104 806 425 (FCI) determinants in C_{2v} symmetry. These computations, as well as the coupled-cluster (CCSDT) procedures, were performed using the PSI package,[34] as linked with the determinant-based configuration interaction program DETCI.[35]

The spectroscopic constants (Table I) were determined by fitting fifth-order polynomials to sets of five energy points tightly converged to $10^{-10}\ E_h$ and uniformly distributed around the best available r_e estimates[4,33] at intervals of 0.005

TABLE II. Comparison of DZP correlation treatments for $X\ ^1\Sigma_g^+\ C_2$ and $X\ ^1\Sigma^+\ CN^+$.[a]

Method	$X\ ^1\Sigma_g^+\ C_2$			$X\ ^1\Sigma^+\ CN^+$		
	E_e	r_e	ω_e	E_e	r_e	ω_e
CISDTQ	−75.724 770	1.2650	1842.5	−91.994 007	1.1975	2000.8
CCSDT	−75.728 136	1.2675	1829.1	−91.998 324	1.1993	1988.4
CI+PT(10^{-5})[b]	−75.729 69	1.268	1875	−91.999 22	1.204	2010
CI+PT(10^{-6})[b]	−75.730 72	1.269	1825	−92.000 81	1.201	1980
CI+PT(10^{-7})[b]	−75.731 38	1.269	1810	−92.001 50	1.202	1970
CISDTQPH	−75.731 495	1.2694	1814.6	−92.001 709	1.2010	1974.5
FCI	−75.731 641	1.2695	1813.4	−92.001 875	1.2012	1973.6

[a]Total energies (E_e) in hartree, equilibrium bond lengths (r_e) in Å, and harmonic frequencies (ω_e) in cm^{-1}.
[b]Reference 4. As described in the text, these energies result from a combination of configuration interaction and perturbation theory applied to internal and external spaces, respectively, partitioned with a second-order energy threshold $\eta = 10^{-n}$.

Å (C_2) or 0.010 Å (CN^+). The quintic coefficient was included under the constraint $f_{rrrrr} = \rho_5 (f_{rrrr})^2/f_{rrr}$ with $\rho_5 = 1.07$, as suggested by a collection of related molecular force field data[36] and broadly supported by the universal Morse oscillator ratio $\rho_5 = 45/49$. Each fifth-order polynomial was then used to determine force constants through fourth order and a complete set of spectroscopic constants[37] [ω_e, B_e, $\omega_e x_e$, $\bar{D}_e$, and α_e] at its interpolated r_e value, which always lay within 0.001 Å of the initial estimate. The estimated quintic term in the polynomials accounts for variations in f_{rrrr} of the order of 1% in shifting the reference point to the interpolated r_e, but it has no bearing on the low-order constants. Starting with the minimum energy values, the force constants (Table I) reproduce to all significant digits the computed energies, which are available at http://zopyros.ccqc.uga.edu/Newpgs/supp_mat.html .

RESULTS AND DISCUSSION

The C_2 and CN^+ species exhibit intricate electronic structures engendered by a near degeneracy of the fifth σ orbital and first π orbital. Spectroscopic probes have established that C_2 has a $^1\Sigma_g^+$ ground state with the primary electronic configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4 (3\sigma_g)^0$, while $a\ ^3\Pi_u$ and $b\ ^3\Sigma_g^-$ states involving …$(1\pi_u)^3(3\sigma_g)^1$ and …$(1\pi_u)^2(3\sigma_g)^2$ configurations lie at $T_e = 716$ and 6434 cm^{-1}, respectively.[38] In the CN^+ case, large internally contracted multireference configuration interaction wave functions computed with correlation consistent basis sets from double- through quintuple-ζ place the lowest $(^1\Sigma^+, ^3\Pi)$ pair of electronic states at $T_e = (0, 880 \pm 100)$ cm^{-1}.[39,40] Whereas the $^1\Sigma^+$ state of CN^+ is well characterized spectroscopically, no triplet systems of CN^+ have been observed to date, leaving experimental uncertainty as to the identity of the ground state. Incorporation of the $C_2[(2\sigma_u)^2 \to (3\sigma_g)^2]$ and $CN^+[(4\sigma)^2 \to (5\sigma)^2]$ pair excitations is paramount to proper zeroth-order descriptions, causing these species to be severe tests for highly correlated single-reference methods. Our exploratory computations have indicated that within the DZP basis, a configuration interaction method must include pentuple substitutions from the Hartree–Fock reference, or the coupled-cluster approach must contain connected triple excitations, to obtain even a

qualitative description of the relative energy differences among the low-lying states of C_2. In the DZP FCI wave functions of $X\ ^1\Sigma_g^+\ C_2$ and $X\ ^1\Sigma^+\ CN^+$, the first five CI coefficients are (0.830, −0.314, −0.094, 0.085, 0.080) and (0.822, −0.300, 0.116, −0.105, 0.092), respectively, which not only highlight the dominant two reference configurations of these systems but also reveal protracted contributions from other important configurations. The widely used $\mathscr{T}_1$ diagnostic[41,42] based on the singles amplitudes of coupled-cluster wave functions confirms the multireference character. In particular, the DZP (CCSD, CCSDT) $\mathscr{T}_1$ values are (0.039, 0.038) for C_2 and (0.062, 0.064) for CN^+, as compared to the suggested single-reference upper limit of 0.02.[42]

Our data for the systematic approach to the FCI limit of truncated single-reference configuration interaction and coupled-cluster spectroscopic constants and total energies are presented in Tables I and II. For (C_2, CN^+) the CISDTQ, CCSDT, and CISDTQPH total energies lie (6.9, 7.9) mE_h, (3.5, 3.6) mE_h, and (0.15, 0.17) mE_h, respectively, above the (FCI) variational limit. For the bond distances and harmonic frequencies, the corresponding [$r_e(C_2)$, $\omega_e(C_2)$; $r_e(CN^+)$, $\omega_e(CN^+)$] discrepancies are [−0.0045 Å, +28 cm^{-1}; −0.0037 Å, +27 cm^{-1}] (CISDTQ), [−0.0020 Å, +16 cm^{-1}; −0.0019 Å, +15 cm^{-1}] (CCSDT), and [−0.0001 Å, +1.2 cm^{-1}; −0.0002 Å, +0.9 cm^{-1}] (CISDTQPH). Thus, the isoelectronic C_2 and CN^+ systems exhibit remarkably consistent behavior; the CISDTQ →CCSDT→CISDTQPH→FCI series of (E_e, r_e, ω_e) values converges from (above, below, above) in a monotonic fashion, with the CCSDT method roughly halving the CISDTQ deficiency and the CISDTQPH level essentially completing the approach to the FCI limit. Accordingly, the exact FCI values support the conclusion of the CI+PT study[4] that the CCSDT method supplies more accurate approximations to the FCI energy, r_e, and ω_e than the CISDTQ level for these two difficult multireference problems. Preferring CISDTQ to CCSDT as a benchmark method[33] may thus be unjustified for systems with eight electrons or more. Nonetheless, Olsen and co-workers[43] have executed an extensive series of 10-electron correlation energy calculations on water in a valence double-zeta basis with polarization functions, finding that at most bond distances the reproduction of FCI energies fol-

lowed   the   sequence   CCSDT<CISDTQ<CCSDTQ <CISDTQPH.

For f_{rrr} and f_{rrrr} the accuracy trends are the same as for E_e, r_e, and ω_e but less systematic, perhaps because bond stretching force constants become increasingly dominated by nuclear–nuclear repulsion rather than electronic effects as the order of the derivative increases.[44] A measure of the balance of the anharmonic force constant predictions for a given level of theory is afforded by the ratio $\rho_4 = f_{rrrr}f_{rr}/(f_{rrr})^2$, which is exactly 7/9 for all Morse oscillators. For C_2 and CN^+, the (CISDTQ, CCSDT, CISDTQPH, FCI) sequence of ρ_4 values is (0.738, 0.754, 0.730, 0.737) and (0.745, 0.743, 0.718, 0.716), respectively. The one result falling outside the anticipated CISDTQ <CCSDT<CISDTQPH$\approx$FCI accuracy trend is that of CCSDT for C_2. In a similar manner, the α_e and $\omega_e x_e$ constants listed in Table I, which generally exhibit the trend observed for all other data, show that CCSDT is aberrant in the C_2 case, being outperformed by CISDTQ due to a poorer balance among higher-order derivatives rather than reduced absolute accuracy in the anharmonic force constants.

Although the focus of the current study is to provide highly correlated predictions of spectroscopic constants within a limited basis, it is worthwhile to compare the theoretical results to the experimentally determined values. The equilibrium bond lengths in C_2 and CN^+ are substantially overestimated at the DZP FCI level, by 0.027 Å and 0.028 Å respectively, and concomitantly the harmonic frequencies are underestimated by 40–60 cm^{-1}. The corresponding errors in α_e and $\omega_e x_e$ range from 1% to 4%. Mitigating the imbalance of the FCI correlation treatment vis-à-vis the limited DZP basis set by employing more approximate correlation methods improves the agreement with experiment, strikingly so in the case of CISDTQ for $\omega_e(C_2)$. However, for the purpose of converging on accurate spectroscopic predictions, a proper theoretical balance should not expand the correlation treatment beyond the (comparatively modest) CCSD method until the basis set is at least of triple-ζ plus ($2d\,1f$) quality.[45–47]

Assessment of Wulfov's CI+PT predictions[4] is effectuated by the data in Table II. The CI+PT(η) energies result from a combination of configuration interaction and perturbation theory applied to internal and external spaces, respectively, and partitioned with a second-order energy threshold $\eta = 10^{-n}$. For (C_2,CN^+) the CI+PT method approaches the FCI energy from above and to an accuracy of (0.26, 0.38) mE_h, while reproducing the FCI r_e and ω_e values to within (0.0005, 0.0008) Å and (3.4, 3.6) cm^{-1}, respectively. The CISDTQ and CCSDT results for E_e, r_e, and ω_e are surpassed by the CI+PT(10^{-6}) predictions, indicating the inclusion of pentuple and hextuple substitutions in the associated selected CI wave functions. These comparisons reveal that the efficient CI+PT scheme is indeed capable of accurate predictions of not only the energy but also spectroscopic constants. (It should be pointed out at the same time that non-size-extensive CI+PT extrapolation schemes may exhibit diminished accuracy for larger systems, a problem not present in any coupled-cluster ansatz for the wave function.) However, for $X\,^1\Sigma_g^+\,C_2$ and $X\,^1\Sigma^+\,CN^+$ a configuration se-

lection threshold less than 10^{-7} appears necessary for the CI+PT FCI estimates to surpass those computed by CISDTQPH. Of course, the computational savings compared to explicit FCI are a distinct advantage of the CI+PT approach. The largest computation reported here (one FCI energy point for CN^+, 105 million determinants) used approximately 75 h, 2 GB of core memory, and 10 GB of disk storage on an IBM RS6000 model 595. In contrast, Wulfov[4] reported that a CI+PT(10^{-8}) computation on the much larger $X\,^1\Sigma_g^+$ F_2 system required about 2 h, 5 MB of core memory, and perhaps a few hundred MB of disk storage on an IBM 486DX2-66 PC.

An important aspect of concern for selected CI schemes is that the potential energy surfaces computed from them will display discontinuities. The frequency, magnitude, and scale at which these irregularities arise is not well documented in the literature. Such aberrant surface features could affect molecular properties computed via central difference techniques, unless the displaced geometries involve the exact set of configurations selected at the initial (nondisplaced) structure. On the other hand, the analytic computation of molecular properties in such schemes should be less affected, since the CI+PT surface corresponding to a (discretely) fixed set of configurations should be smooth and differentiable. In this respect it seems that explicit FCI benchmark data for higher-order force constants should aid the development of both accuracy and smoothness criteria for selected CI methods and their correlation extrapolations. Accordingly, the reproduction of the anharmonic data for C_2 and CN^+ obtained here (Table I) is elevated as a goal for future work.

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